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Consideration of Kaolinite Interference Correction for Quartz Measurements in Coal Mine Dust

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Abstract

Kaolinite interferes with the infrared analysis of quartz. Improper correction can cause over- or underestimation of silica concentration. The standard sampling method for quartz in coal mine dust is size selective, and, since infrared spectrometry is sensitive to particle size, it is intuitively better to use the same size fractions for quantification of quartz and kaolinite. Standard infrared spectrometric methods for quartz measurement in coal mine dust correct interference from the kaolinite, but they do not specify a particle size for the material used for correction. This study compares calibration curves using as-received and respirable size fractions of nine different examples of kaolinite in the different correction methods from the National Institute for Occupational Safety and Health Manual of Analytical Methods (NMAM) 7603 and the Mine Safety and Health Administration (MSHA) P-7. Four kaolinites showed significant differences between calibration curves with as-received and respirable size fractions for NMAM 7603 and seven for MSHA P-7. The quartz mass measured in 48 samples spiked with respirable fraction silica and kaolinite ranged between 0.28 and 23% (NMAM 7603) and 0.18 and 26% (MSHA P-7) of the expected applied mass when the kaolinite interference was corrected with respirable size fraction kaolinite. This is termed “deviation,” not bias, because the applied mass is also subject to unknown variance. Generally, the deviations in the spiked samples are larger when corrected with the as-received size fraction of kaolinite than with the respirable size fraction. Results indicate that if a kaolinite correction with reference material of respirable size fraction is applied in current standard methods for quartz measurement in coal mine dust, the quartz result would be somewhat closer to the true exposure, although the actual mass difference would be small. Most kinds of kaolinite can be used for laboratory calibration, but preferably, the size fraction should be the same as the coal dust being collected.

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Keywords

coal dust; FTIR; kaolinite; NMAM 7603; P-7; quartz; silica

INTRODUCTION

Currently, several standard infrared (IR) spectrometric methods are available in the United States for quartz mass measurement in coal dust, including the National Institute for Occupational Safety and Health (NIOSH) *Manual of Analytical Methods* (*NMAM*) 7602 Silica, Crystalline by IR (KBr pellet),[(1)] 7603 Quartz in coal mine dust, by IR (redeposition),[(2)] and Mine Safety and Health Administration (MSHA) P-7 (Infrared determination of quartz in respirable coal mine dust).[(3)] The Mine Safety and Health Act of 1977 requires assessment of exposure to respirable crystalline silica for protection of coal miners' health. Approximately 15,000 samples are analyzed annually by the MSHA Pittsburgh laboratory staff according to the MSHA P-7 method.[(4)] Initially, quartz mass collected on filters was determined by IR spectrometry with potassium bromide pellet (NMAM 7602), and any kaolinite interference was ignored until publication of a relevant report from the Stanford Research Institute (SRI)[(5)] that described the kaolinite interference. Kaolinite is the only mineral commonly found in coal mine dust that interferes with IR analysis of quartz,[(6)] resulting in a possible over- or underestimation of quartz exposures if a proper correction for its presence is not made.

The NMAM 7603 and MSHA P-7 methods are basically the same method but use different procedures to correct for interference of kaolinite, i.e., peak height and peak area measurement, respectively. The current versions of the NMAM 7603 and MSHA P-7 analyze respirable quartz by its characteristic IR absorptions near 800 cm^{-1}, and interference due to kaolinite is characterized by the ratio of absorbance at 800 and 915 cm^{-1}; i.e., the kaolinite absorbance at 915 cm^{-1} is proportional to its interfering absorbance at 800 cm^{-1}. The NMAM 7603 and MSHA P-7 adjust for the overlap of kaolinite absorbance at the quartz 800 cm^{-1} by specifying that the method be calibrated via standard samples with kaolinite. A standard reference material (SRM) for respirable α-quartz (1878a) from the National Institute of Standards and Technology (NIST) is available for the quartz calibration, and there were significant difference in relative recovery and precision between the laboratories using (recovery 0.97; standard deviation 0.16) and not using SRM (recovery 1.08; standard deviation 0.30).[(7)] However, an SRM for the kaolinite is currently not available. The NMAM 7603 and MSHA P-7 methods specify Hydrite UF from Georgia Kaolin as standard kaolin, but the Hydrite UF has not been commercially available for a decade. Even if Hydrite UF kaolin is available as a standard, there remain questions about its suitability in its "as-received" form.

A truly representative standard respirable dust for IR analysis should not only be chemically pure, it should also be the same size as the material being measured, i.e., respirable size. This is because of the particle size effect on IR absorption intensity; the absorbance per mass of material is less intense for large particles compared to small ones. This effect is particularly pronounced for dust particles in the respirable size range.[(8–10)] However,

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commercial sources of kaolinite usually do not specify particle size distribution and common practice has been to ignore this complication. It is the intention of this study to demonstrate the effect of particle size on kaolinite calibration.

This study compares calibration curves of eight different commercially available kaolinites and Hydrite UF in asreceived distributions (total kaolinite powder from manufacturers) and their respirable size fractions in order to provide more realistic interference correction for quartz measurement in coal mine dust. This study also compares the two different kaolinite correction methods used by NIOSH and MSHA.

METHODS

Collection of Respirable Size Fraction Kaolinite

Eight different commercially available kaolinites and Hydrite UF were obtained, and a summary is shown in Table I. Each as-received kaolinite was dispersed from a fluidized bed aerosol generator (Model 3400; TSI Inc., Shoreview, Minn.) through a Kr-85 aerosol neutralizer (Model 3012A, TSI Inc.) into a calm air chamber that was previously validated for spatial variability.[11,12] Bed flow in the fluidized bed aerosol generator was maximized to aerosolize larger particles. Respirable size fractions of kaolinite were collected with GK2.69 cyclones (BGI Inc., Waltham, Mass.) loaded with polycarbonate filters (0.2 μm pore size; Millipore, Billerica, Mass.), and the collected particles were extracted from the filter using isopropyl alcohol and sonication. The extraction liquid was centrifuged and the supernatant excess isopropyl alcohol was decanted. The remaining absorbed alcohol was evaporated from the collected particles by air drying before storage.

Dosing Filters

To make a sample, a 25-mm glass fiber filter was placed on a fritted base and two 25-mm DM Metricel membrane filters (DM450, 0.45 μm, 25 mm; PALL Life Sciences, Ann Arbor, Mich.) were placed on the top of the glass fiber filter. The two 25-mm Metricel membrane filters were made from a single 47-mm DM-450 filter from which two circular pieces were cut. The two pieces were stacked so that the second piece could serve as a background to the top piece for Fourier Transform Infrared (FTIR) analysis; the bottom piece was therefore treated with alcohol and vacuumed identically to the top but did not capture any particulate. After setting up a custom-made 10-mm-diameter funnel, isopropyl alcohol was added to the funnel prior to adding sample from the suspension.

Calibration Curve Construction

A calibration curve for quartz was constructed by following the NMAM 7603[2] using respirable α-quartz (NIST-certified SRM 1878a). Eight different masses of quartz were prepared with a range from 10 to 300 μg. A calibration curve for kaolinite as an interference dust in quartz analysis was also constructed following NMAM 7603. As-received total kaolinite powder from manufacturers and respirable size fractions of kaolinite (prepared as described above) were equilibrated in a weighing facility (as described in Lee et al.)[13] for a minimum of 72 hr, and the mass of kaolinite was measured to make 0.1 mg/mL suspension of kaolinite in isopropyl alcohol. Nine different masses from 20 to 750 μg of calibration

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samples were deposited on DM-450 filters. After deposition the pair of 25 mm DM-450 filters was placed in a petri dish to air dry. Both background and sample filters were analyzed with an FTIR (Nicolet 6700; Thermo Fisher Scientific, Waltham, Mass.) spectrometer.

FTIR Analysis

Absorbance of the quartz was quantified by two different methods: (1) the NMAM 7603 method was used to measure the peak height of the absorbance band at 800 cm^{-1} with a baseline between 820 and 670 cm^{-1}, and (2) the MSHA P-7 method was used to measure the absorbance peak area with a baseline between 815 and 770 cm^{-1}. The absorbance of kaolinite was also quantified by two different methods: (1) the NMAM 7603 method was used to measure the peak height of the absorbance band at 915 cm^{-1} with a baseline between 960 and 860 cm^{-1} and the peak height of the absorbance band at 800 cm^{-1} with a baseline drawn between 820 and 670 cm^{-1}, and (2) the MSHA P-7 method was used to measure the absorbance peak area with baselines between 930 and 900 cm^{-1} and between 815 and 770 cm^{-1}. All absorbances were measured using the Omnic software package (version 8.1.11; Thermo Fisher Scientific). The baseline of each method is shown in Figure 1. A calibration curve of respirable α-quartz was constructed with masses (from volume of suspension in isopropyl alcohol) of SRM 1878a using IR absorbance at 800 cm^{-1}. Calibration curves for kaolinites were constructed with IR absorbance at 800 (abscissa) and 915 (ordinate) cm^{-1}. Calibration curve equations and regression coefficients (R^2) were calculated using a linear regression analysis.

Size Distribution Measurement

The number size distributions of each kaolinite were measured using a Multisizer 3 Coulter counter (size range: 2–60 μm; Beckman Coulter Inc., Brea, Calif.) to compare size distribution of as-received and respirable size fractions. Each size fraction of kaolinite suspension was sonicated for 20 min and stirred by a magnetic stirrer. While stirring the suspension, 1 ml of kaolinite suspension was added to 5-mL saline solution.

Spiked Samples

Forty-eight different samples spiked with varying levels of 1878a and six different respirable size fraction kaolinites were prepared from Kaolinites #1, 3, 4, 6, 7, and 8. Kaolinites #2 and 5 were not used because their calibration curves are significantly different from the others, and Kaolinite #9 was not used since it is not commercially available. Filters spiked with aliquots of standard solutions to deposit quartz masses between 15 and 45 μg and kaolinite masses between 10 and 750 μg (calibration curve mass range) were characterized by both the NMAM 7603 (peak height) and MSHA P-7 (peak area) methods. Quartz masses were determined by correcting kaolinite interference using both as-received and respirable size fraction calibration curves. The difference between quantified quartz mass with kaolinite correction and quartz mass calculated with volume of quartz suspension is recorded as a percentage deviation

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$$\left(\frac{|Quartz\ mass\ from\ calibration\ curve\ with\ kaolinite\ correction\ -\ spiked\ quartz\ mass\ calculated\ f}{|Spiked\ quartz\ mass\ calculated\ from\ volume\ of\ suspension|}\right.$$

assuming the applied mass is a “true” value, even though it is subject to unknown variance. Differences between the calibrations in the deviation were compared using respirable and as-received fraction kaolinites.

Statistical Analysis

All analyses were generated using SAS/STAT software, version 9.2 of the SAS system for Windows (SAS Institute, Cary, N.C.). All differences were considered significant at $p < 0.05$. Equality of calibration slopes for each kaolinite was assessed using PROC MIXED to run a two-way factorial analysis of variance with the absorbance at 915 cm^{-1} as the dependent variable and the absorbance at 800 cm^{-1} as a continuous independent variable along with reading method as a categorical independent variable. (There were two methods of reading peak intensity, either peak height above background or peak area with background area subtracted.) Significant interactions indicated unequal slopes. Comparison of slopes between kaolinite types was assessed using a two-way factorial with kaolinite type as a categorical variable within each method and fraction. Percentage deviations from spiked samples calculated under the various methods were analyzed with a threeway factorial analysis of variance (ANOVA) using fraction, method, and mass of kaolinite as the independent variables. The significant three-way interaction was further assessed using two-way factorials for each fraction. Pairwise differences were assessed using Fisher’s Least Significant Difference test.

RESULTS

Calibration Curves for As-Received and Respirable Size Fraction Kaolinites

Linear calibration curve equations (FTIR absorbance 800 cm^{-1} vs. 915 cm^{-1}) and regression coefficient (R^2) determined by peak height and peak area methods for nine different kaolinites are shown in Table II. The equations determined by the peak height for respirable size fraction of Kaolinites #1(a typical kaolin), #2 (halloysite nanoclay), and #5 (acid washed clay powder) were significantly different from other kaolinites ($p < 0.05$), and the equations from peak area method produced the same results (Figure 2). Calibration curves of Kaolinites #1, 2, 5, and 8 showed significant differences between asreceived and respirable size fraction with peak height method, but Kaolinites #3, 4, 6, 7, and 9 did not. Calibration curves of Kaolinites #1, 2, 4, 5, 6, 8, and 9 showed significant differences between as-received and respirable size fraction with peak area measurement. The slopes of calibration equation from respirable size fraction with peak height method were larger than those from as-received fraction in most of the kaolinites (except Kaolinite #8), while the slopes of calibration equation from respirable size fraction with peak area method were larger than those from as-received fraction in all kaolinites.

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Size Distribution Measurement

The cutoff sizes (d_{10}, d_{50}, d_{90}) of each kaolinite were measured with a Multisizer 3 Coulter counter (Beckman Coulter Inc.) for as-received and respirable size fractions as shown in Table III. All cutoff sizes of as-received fractions are larger than those of the corresponding respirable size fractions. The number size distributions of Hydrite UF (Kaolinite #9) for as-received and respirable size fractions are shown in Figure 3. The regression coefficient and 95% confidence intervals of an exponential distribution of each kaolinite size fraction were calculated and relevant comparisons of overlapping in the confidence intervals around coefficient were checked. Significant difference was found between the number size distribution of as-received and respirable size fractions from all kaolinites.

Spiked Samples

A list of the respirable α-quartz and respirable kaolinite mass loadings in 48 different spiked samples and their quartz masses calculated using the calibration equations of as-received and respirable size fraction of kaolinite are shown in Table IV. The deviations of measured quartz mass from applied quartz mass in the 48 quartz and kaolinite spiked samples ranged between 0.28 and 23% (peak height measurement) and 0.18 and 26% (peak area measurement) when kaolinite interference was corrected with the calibration curve of respirable size fraction kaolinite. The deviations of measured quartz mass from applied quartz mass were generally larger when the calibration curves of as-received size fraction kaolinite were used; the deviation ranges of spiked samples with as-received kaolinite calibration curve were between 0.06 and 45% (peak height measurement) and 0.19 and 87% (peak area measurement). There are no statistically significant differences in deviations between measurement by peak height and peak area measurement for the respirable size fractions, while the deviations measured by the peak height method are significantly lower than those measured by the peak area method for the as-received size fraction.

DISCUSSION AND AN ADDITIONAL EXPERIMENT

Calibration curves of nine different kaolinites in two different size fractions were investigated. The calibration equations based on the two distinct size distributions differed significantly for some of the kaolinites. Different sizes of kaolinite yield different calibration equations because their absorption intensities per mass differ according to particle size; in particular, it is the ratio of the absorbances at 800 and 915 cm^{-1} band (Figure 4) that is used to define the calibration equations. The absorbance difference between as-received and respirable size fractions at 800 cm^{-1} was relatively smaller than the absorbance difference at 915 cm^{-1} since the absorbance of 915 cm^{-1} was approximately 8 times larger than 800 cm^{-1} for most kaolinites by the peak height method.

The dependence of intensity on particle size seen here may arise for one or more reasons. First, these two peaks are assigned to Si-O and OH deformation of inner hydroxyl groups, respectively.[14] As the particle size is decreased, absorbance of Si-O and OH deformation of inner hydroxyl groups per unit mass is increased due to increased surface area of the particles. Second, it is known that particle size has an influence on IR absorbance.[8,9] Foster and Walker[10] investigated particle size effects for quartz infrared absorbance using a

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cascade impactor to separate the quartz particles. They report that the absorbance of 100 μg quartz of median diameter 3.75 μm was twice that of the same mass of 5.20 μm median diameter at 799 cm^{-1}. The IR absorbance ratio between 1.70 μm and 8.1 μm median diameters was greater than three in their experiment.

Similar findings (but for kaolinite) are reported in the present study; i.e., respirable size fractions (smaller size particles) showed larger FTIR absorbance per mass than as-received size fractions, with one exception, Kaolinite #8 by the peak height method. This could be attributed to the larger peak height around 670 cm^{-1} of as-received size fraction only, which band is acting as baseline for peak height measurement at 800 cm^{-1}; consequently, the ratio between 915 to 800 cm^{-1} is larger compared to other kaolinites. The peak area method showed the same result as the other kaolinites since peak area does not use 670 cm^{-1} as the end of the baseline.

Kaolinites #2 and 5 showed significantly different calibration slopes relative to the other kaolinites. Since Kaolinite #2 is halloysite, it has a structure similar to kaolinite but frequently contains water between the tetrahedral and octa- hedral sheets, consequently containing more hydroxyl groups per unit mass that contribute more intensity to the hydroxyl absorption bands, a result consistent with the present study (Figure 2; Kaolinite #2 has larger slope equation than other kaolinites).

By way of counter-example, there is Kaolinite #5, an acidwashed powdered kaolinite. The acid treatment removes aluminum from the structure and also reduces considerably the number of inner hydroxyl groups per unit mass.[15] This modification should decrease the number of hydroxyls per mass and, hence, should decrease the slope of the calibration curve relative to untreated kaolinite, consistent with what is shown in Figure 2. The NMAM 7603 and MSHA P-7 methods specified Georgia kaolin, Hydrite UF as a standard material for calibration with a presumption that the material was in the respirable size range, although this is not specifically stated. This product, however, was discontinued 8 years ago and is no longer commercially available. There is no NIST standard reference material for kaolinite currently available.

A prior collaborative study[5] with over 30 laboratories, including NIOSH, SRI, and the U.S. Bureau of Mines investigated methods for silica measurement with IR and XRD. The standard kaolinite for this study was Hydrite UF with a median particle size that was reported as 0.2 μm by the manufacturer.[16] The study used respirable size fraction for determining the kaolinite calibration curve. That study re-ported a slope of the kaolinite IR absorbance between 800 and 915 cm^{-1} to be 7.41, close to that seen in the present study, 7.58.

In our previous study regarding quartz measurement in coal mine dust with high flow rate samplers,[11] Pittsburgh coal dust was aerosolized in a calm air chamber and coal dust was collected with five different respirable size selective samplers. When the quartz mass concentration was calculated with as-received and respirable size fractions of Kaolinite #8, the quartz mass differences between the two different size fractions were found to be approximately 4.5% ± 1.6 (n = 90). The quartz mass differences between the two fractions,

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when calibration curves of Hydrite UF were applied, were approximately 1.5% ± 0.5. The mass ratio of kaolinite to quartz in that coal mine dust was determined to be 0.25 ± 0.27. If the mass ratio of kaolinite to quartz is increased in coal dust, then the mass concentration difference between as-received and respirable size fraction kaolinite interference correction would be increased. The respirable size fraction is collected in industrial hygiene practice for exposure assessment and calibration for IR measurement should therefore be with respirable size fraction in the laboratory.

Another experiment was conducted to address requirements of the Methods for the Determination of Hazardous Substances 101 (MDHS, Crystalline silica in respirable airborne dusts) from the Health and Safety Laboratory, U.K.[17] MDHS 101 recommends quartz on reference filters be prepared from airborne particles by using a dust cloud generator rather than by suspension of quartz in isopropyl alcohol. This recommendation ensures that the standard reference sample will have approximately the same particle size distribution as the sample under consideration. Airborne calibration samples for Kaolinite #8 were collected on PVC filters (GLA5000; SKC Inc., Eighty Four, Pa.) using GK 2.69 (seven different masses) and 10-mm nylon (eight different masses) cyclones in a calm air chamber, and the filters were ashed in a Plasma-Prep II (Model 11005; SPI Inc., West Chester, Pa.) for a minimum of 2 hr to eliminate organic material from the samples. The ashed sample was deposited on a DM Metricel membrane filter for FTIR analysis. Their calibration slopes with absorbance between 800 and 915 cm^{-1} were similar; y = 7.503x for GK2.69 cyclone, y = 7.649x for 10-mm nylon cyclone, y = 7.749x for suspension of Kaolinite #8 in isopropyl alcohol. These results are not significantly different ($P > 0.05$) from each other.

CONCLUSION

Calibration curves of the respirable and as-received size fractions in nine different kaolinites were investigated using two current standard methods, NMAM 7603 and MSHA P-7. More than half the kaolinites showed significant differences in FTIR absorbances between the two different size fractions, mainly due to the size effect. These results indicate that if a kaolinite correction with standard reference material with respirable size fraction is applied in current standard methods for quartz measurement in coal mine dust, it would likely be closer to the true exposure although the quartz mass difference between two size fractions' correction is small. The methods from NIOSH 7603 (peak height) and MSHA P-7 (peak area) did not show significant differences in the deviations from kaolinite corrected spiked samples. Most kinds of kaolinite can be used for laboratory calibration, but preferably, the size fraction should be the same as the coal dust being collected.

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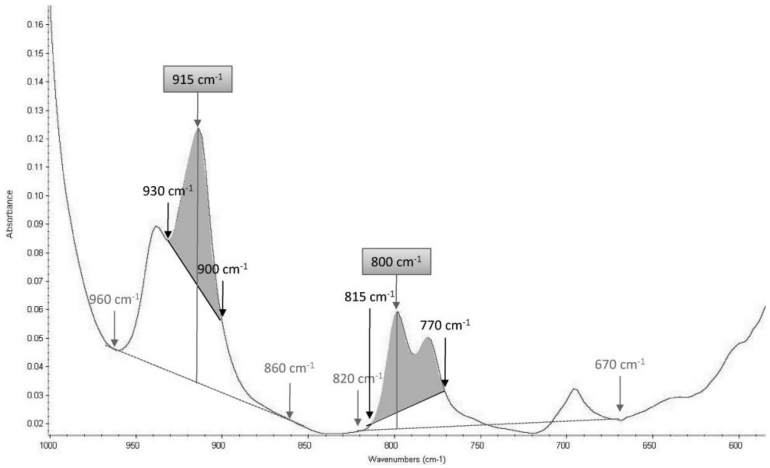

FIGURE 1.

FTIR spectrum measurement of kaolinite in NIOSH Manual of Analytical Method 7603 (peak height measurement; baseline 960−860 cm^{-1} and 820−670 cm^{-1}) and MSHA P-7 (peak area measurement; baseline 930−900 cm^{-1} and 815−770 cm^{-1})

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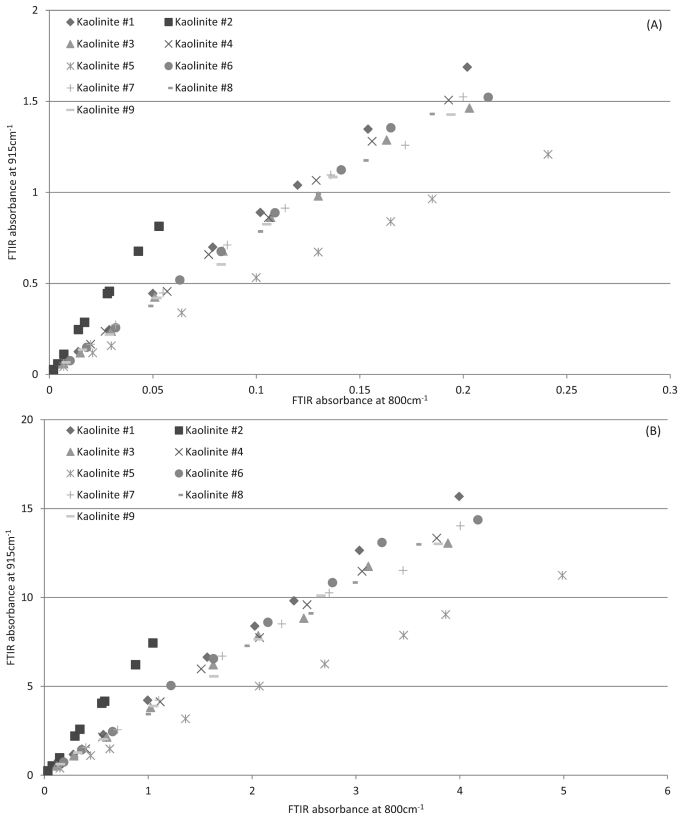

FIGURE 2.

Calibration curves (FTIR absorbance at 800 cm^{-1} vs. 915 cm^{-1}) of respirable fraction of kaolinites by (A) peak height and (B) peak area methods

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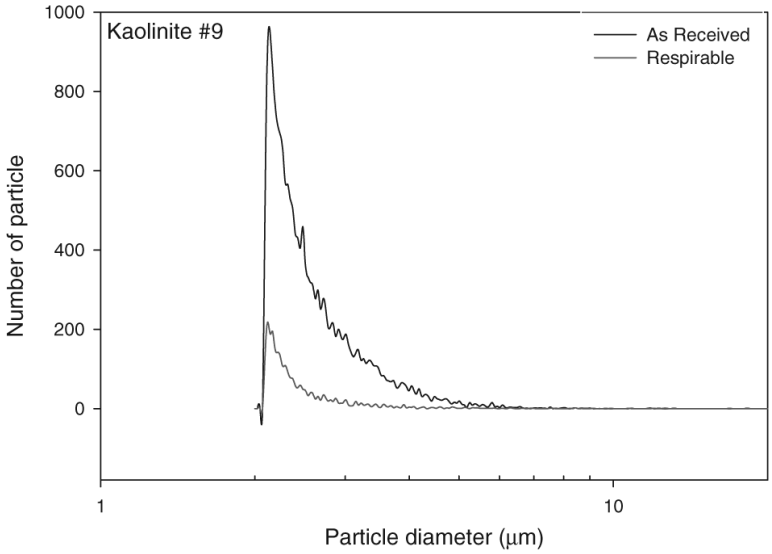

FIGURE 3.

Number size distribution of Hydrite UF (Kaolinite #9) for as-received and respirable size fractions determined with Multisizer 3 Coulter counter

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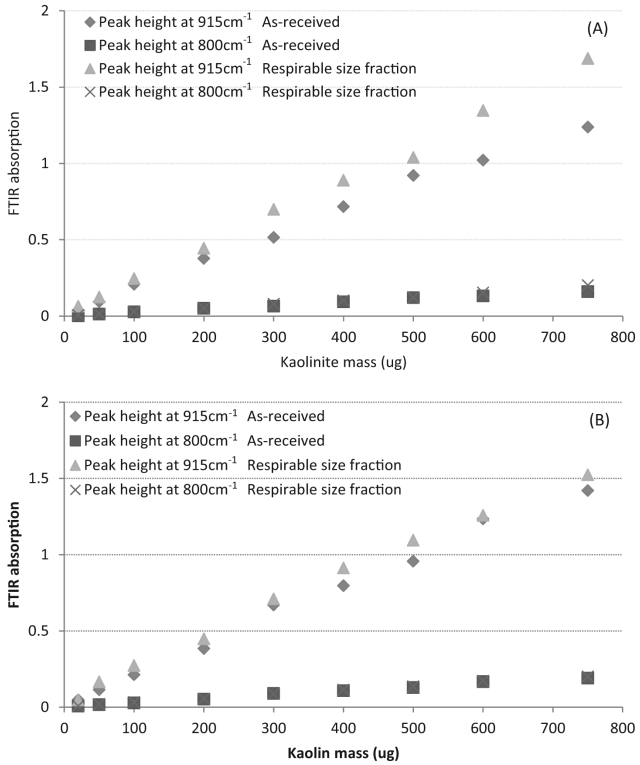

FIGURE 4.

FTIR absorbance of Kaolinite #1 (A) and #7 (B) at 915 and 800 cm^{-1} for two different size fractions

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TABLE I

Summary of Kaolinites Used in the Study

Kaolinite	Manufacturer	Description
1	Fluka Analytical	Product of Germany
2	Aldrich Chemistry	Halloysite kaolin nanoclay, product of United States
3	Sigma-Aldrich	Hydrated aluminum silicate bolus, product of United States, meets requirements from USP[A]
4	Sigma-Aldrich	Hydrated aluminum silicate bolus product of United States
5	Fisher Scientific	Acid-washed powder, product of United States
6	Across Organic	Kaolin, product of Belgium
7	JT Baker	Product of United States, meets requirement from USP
8	The Clay Minerals Society	Washington County Georgia, KGa-1b (replaces KGa-1, contains 1–2% of quartz)
9	Imerys	Hydrite UF Standard material for NAM 7603 and P-7 methods; Georgia kaolin, no longer commercially available

[A]USP: US Pharmacopeial Convention.

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TABLE II

Calibration Curve Equations and Regression Coefficients of As-Received and Respirable Fraction of Kaolinite

	Peak Height Method (NMAM 7603)				Peak Area Method (P-7)			
	As-Received		Respirable		As-Received		Respirable	
	Slope Equation	R^2	Slope Equation	R^2	Slope Equation	R^2	Slope Equation	R^2
1	7.721[A]	0.999	8.575	0.999	3.100[A]	0.997	4.058	0.998
2	14.289[A]	0.998	15.687	0.997	5.211[A]	0.995	7.159	0.999
3	7.739	0.998	7.609	0.993	3.398	0.999	3.580	0.991
4	7.996	0.999	8.072	0.997	3.378[A]	0.999	3.685	0.996
5	2.600[A]	0.999	5.116	0.999	1.373[A]	0.997	2.298	0.999
6	7.085	0.999	7.758	0.989	2.979[A]	0.999	3.776	0.984
7	7.442	0.999	7.721	0.995	3.320	0.999	3.561	0.992
8	9.122[A]	0.995	7.750	0.999	3.318[A]	0.999	3.630	0.999
9	7.233	0.990	7.584	0.996	3.297[A]	0.986	3.565	0.994

[A]Significantly different between as-received and respirable size fraction kaolinite calibration curves ($p < 0.05$).

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TABLE III

Cutoff Sizes of Kaolinites for As-Received and Respirable Size Fractions Measured by a Multisizer 3 Coulter Counter

		Cutoff Size (μm)		
Kaolinite	**Size Fraction**	**d_{10}**	**d_{50}**	**d_{90}**
#1	As-received	2.17	2.62	4.68
	Respirable	2.14	2.32	3.00
#2	As-received	2.18	2.67	4.57
	Respirable	2.14	2.36	3.01
#3	As-received	2.15	2.45	3.77
	Respirable	2.13	2.30	2.94
#4	As-received	2.16	2.51	3.86
	Respirable	2.13	2.30	2.94
#5	As-received	2.15	2.51	4.77
	Respirable	2.12	2.28	2.95
#6	As-received	2.16	2.64	6.12
	Respirable	2.15	2.42	3.47
#7	As-received	2.15	2.47	3.90
	Respirable	2.13	2.28	2.87
#8	As-received	2.16	2.53	4.13
	Respirable	2.13	2.25	2.71
#9	As-received	2.14	2.42	3.45
	Respirable	2.13	2.29	3.09

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TABLE IV

Spiked Samples Loaded with Respirable α-Quartz and Kaolinite

				Quartz Mass from Peak Height (μg)		Quartz Mass from Peak Area (μg)	
Sample Number	1878a mass (μg)	Kaolinite	Kaolinite Mass (μg)	As-Received	Respirable	As-Received	Respirable
1	15	1	10	16.12	16.32	15.08	15.70
2	15	3	10	14.99	14.96	14.68	14.82
3	15	4	10	15.71	15.72	15.10	15.20
4	15	6	15	15.57	16.01	14.10	15.47
5	15	7	15	14.42	14.54	13.46	13.73
6	15	8	15	15.53	15.24	14.50	14.73
7	15	1	15	14.61	14.87	13.90	14.68
8	15	3	30	13.55	13.48	13.24	13.53
9	15	4	30	15.83	15.90	14.48	15.16
10	15	6	30	13.48	14.02	12.43	14.07
11	15	7	30	14.88	15.07	13.74	14.21
12	15	8	30	15.03	14.39	13.65	14.10
13	30	1	20	29.06	29.53	28.07	29.61
14	30	3	20	28.95	28.91	28.17	28.37
15	30	4	20	28.03	28.07	27.33	27.69
16	30	6	30	29.68	30.36	28.13	30.14
17	30	7	30	27.77	27.95	27.08	27.49
18	30	8	30	33.44	32.78	30.85	31.34
19	30	1	30	30.55	31.02	28.59	30.10
20	30	3	30	29.01	28.94	27.99	28.31
21	30	4	45	28.92	29.00	27.69	28.45
22	30	6	45	27.85	28.56	26.36	28.51
23	30	7	45	32.96	33.23	30.19	30.79
24	30	8	45	31.67	30.69	26.30	27.04
25	45	1	30	43.00	43.61	40.50	42.38
26	45	3	30	42.36	42.30	40.54	40.83
27	45	4	30	46.01	46.05	45.10	45.52
28	45	6	45	43.80	44.70	40.17	42.93
29	45	7	45	41.34	41.77	40.39	41.35
30	45	8	45	45.48	44.50	44.38	45.08
31	45	1	45	41.91	42.57	39.18	41.28
32	45	3	45	40.21	40.11	38.68	39.10
33	45	4	60	42.08	42.16	38.85	39.68
34	45	6	60	45.70	46.60	43.51	46.24
35	45	7	60	49.04	49.37	47.43	48.16
36	45	8	60	45.29	44.10	42.49	43.32
37	30	1	100	24.54	26.03	21.45	26.04

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Sample Number	1878a mass (μg)	Kaolinite	Kaolinite Mass (μg)	Quartz Mass from Peak Height (μg)		Quartz Mass from Peak Area (μg)	
				As-Received	Respirable	As-Received	Respirable
38	30	3	200	27.27	26.86	27.72	29.36
39	30	4	300	27.17	27.56	22.97	26.83
40	30	6	400	16.55	23.07	3.89	23.70
41	30	7	500	22.21	24.85	16.45	22.22
42	30	8	600	36.78	24.60	21.53	29.40
43	45	1	600	32.12	39.87	13.55	37.77
44	45	3	750	36.99	35.52	27.16	33.16
45	45	4	400	42.76	43.28	37.13	42.30
46	45	6	500	30.85	37.50	16.56	36.79
47	45	7	600	34.95	38.01	28.17	34.82
48	45	8	600	50.68	39.20	35.82	43.27